PATENT SPECIFICATION (11) 1 604 405

1 604 405

(21) Application No. 35499/77 (22) Filed 24 Aug. 1977
(21) Application No. 46826/77 (22) Filed 10 Nov. 1977
(23) Complete Specification filed 31 May 1978
(44) Complete Specification published 9 Dec. 1981
(51) INT CL³ C08K 3/00; C08F 2/44; C08K 3/40
(52) Index at acceptance
C3K 111 400 MA
C3W 100 228 304 328
C3Y B165 B180 B183 B184 B262 B263 B270 B405

(72) Inventors ROBERT JAMES BREAKSPEARE, PHILIP JAMES HEATH and JOHN CLIVE JONES

# (54) IMPROVEMENTS IN AND RELATING TO ARTICLES MADE FROM RESIN COMPOSITIONS CONTAINING AGGREGATE MATERIALS, E.G. GLASS

(71) We, UNIVERSITY COLLEGE CARDIFF, of P.O. Box 78, Cardiff, CF1 1XL, and GLASS MANUFACTURERS FEDERATION, of 19, Portland Place, London, W1N 4B11, a British University and a British Company respectively, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to articles made from a composition containing material in aggregate (as herein defined) form disposed within a matrix.

In recent years much concern has been expressed about the vast quantities of potentially useful materials discarded in domestic and industrial refuse. Such waste materials include vitreous materials, e.g. glass, porcelain and vitreous enamel waste; clay materials, e.g. china clay, brick waste and pumice; foundry waste, e.g. mould slag, mould sand and fuel ash, and slate waste. Nationally, it is generally accepted that between 1.5 and 2.0 million tons of glass are discarded in domestic refuse each year. The glass is usually derived from bottles, jars etc., and where it forms part of a mixed refuse, it is separated therefrom using a special separation plant prior to ultimate disposal.

It is an object of this invention to turn waste glass and other materials such as those indicated above into a composition which can be usefully employed in the manufacture of structural, decorative and other articles, for example, tiles, curtain walling, decorative/structural panels, sanitary ware, pipes etc. The composition of the invention may be cast, moulded or otherwise formed into desired shapes. The composition may also be used, in plastic form, as floor covering which, when cured, is ground and subsequently polished.

According to this invention a method of preparing an article from a composition comprises:

(a) formulating a mixture of coarse, medium and fine aggregates (as herein defined);
(b) pretreating the mixture (a) with a coupling agent;
(c) mixing the pretreated mixture (of (b)) with a curable resin and a curing catalyst for curing the curable resin, and
(d) forming the resulting mixture (of (c)) into an article and curing or allowing the same to cure.

Where the aggregate is glass, the curing temperature may be in the region of 105°C.

If desired, there may be added to the mixture (a) a further mixture comprising a weighed quantity of fine aggregate (as herein defined), pretreated with a coupling agent, polymer, polymerisation and/or colouring agents and a curing catalyst.

Throughout this specification, by coarse, medium and fine aggregates, we mean aggregates falling within the following size ranges, namely,

coarse: up to 3 BS mesh (0.75—0.25 inch or 19 to 6.35 mm);
medium: 3 to 12 BS mesh (6.35—1.40 mm), and
fine: greater than 12 BS mesh and preferably greater than 85 BS mesh (0.180 mm = 85 BS mesh).

In the case of glass aggregate, bottles (and other glass articles) may be crushed in a jaw crusher to obtain the coarse fraction of glass. Labels and metal rings need not be removed although caps and corks are preferably removed. Further the bottles need not be washed prior to crushing. The coarse fraction of approximately 0.75—0.25 inch (19 mms—6.35 mms) is, as mentioned above, screened from the jaw crusher product and, thereafter, a proportion of the coarse fraction may, by using for example a combination of disc mills, be ground still further to produce the medium and fine fractions.

The fine fraction as indicated above is preferably finer than 85 mesh (0.180 mms) and, if desired, material of industrial origin may be used as the fine fraction consisting for example of glass dust obtained from air conditioning filters. Occasionally this fine size range is modified or omitted to achieve particular surface effects.

Each fraction and each colour is preferably kept separate in order to give flexibility in formulation, colour and colour effects.

Where the invention is used to make tiles, the tile mix is formulated from the aggregate fractions as defined above in the following approximate proportions by weight:

Coarse: 44.3%;
Medium: 26.5%; and
Fine: 29.2%

and this mix results in a void volume of approximately 0.22—0.24%.

A charge of glass to the above specification (suitably selected for the desired colour effect) is weighed out into a mixing vessel in preparation for the pretreatment of stage (b).

The preferred pretreatment or coupling agent is a trimethoxy silane marketed by Dow Corning Ltd. Another coupling agent which may be used is VOLAN (Registered Trade Mark) — a chrome/acrylic complex made by Firth Chemical Company of Crewe. The pretreatment solution contains typically 0.2% w/w of silane in water and the volume of treating solution is such as to give typically 0.5% w/w of silane to glass. The pH of the solution is adjusted to within the range of 4—6 with the addition of acetic acid and stirred with the glass aggregate charge for 15 minutes. This stage may be prolonged as necessary since it serves the double purpose of pretreating the glass aggregate and removing the remains of labels. The aqueous solution is then decanted-off and the glass dried at a temperature of 105°C.

The dried glass is then cooled or allowed to cool and mixed with a curable resin system. This charge gives typically a glass to resin ratio of 4.0 to 8.0.

Immediately prior to pouring into a mould, the catalyst and promoter charges are added and thoroughly mixed with the glass/resin mix. A mix to this formulation prepared with a polyester as described later in Example 1 was found to have a compressive stress of 10925 lbs./sq. inch.

Ideally, the mix is poured into the mould and thoroughly 'trowelled' with a palette knife to fill every corner, recess etc., of the mould, and to expel every air bubble from the bottom of the mould where the surface of the finished tile is formed. Carrying out this operation on a vibrating table greatly helps to produce a good surface and homogeneous product.

The mould determines the size and thickness of the finished tile, for example, open moulds measuring 7" × 7" × 5/8" made of silicone rubber and of 9" × 9" × 3/8" aluminium have been found very satisfactory. The mould is laid on a flat surface and it is the flat surface which gives the finished tile its surface quality.

A glass sheet, highly polished with an ordinary silicone-free wax polish such as Mansion Wax (Trade Mark) gives a reasonable mould release and a very high surface gloss to the tile.

A glass sheet coated with paraffin wax affords good release properties and a flat matt surface which gives good wet skid resistance.

Exceptionally good mould release is however obtained by casting onto a thin sheet of "Teflon" (Registered Trade Mark) supported on a sheet of flat glass and gives rise to a medium glass surface.

The invention will now be illustrated with reference to the following examples:

EXAMPLE 1.

Glass obtained from a brewery was crushed and sizes as previously detailed and a tile mix was formulated as follows:

| | | |
|---|---|---|
| Coarse (green) | 443g | (44.6%) |
| Medium (brown) | 316g | (31.8%) |
| Fine (white) | 234g | (23.6%) |

This mixture was pretreated as described with a trimethoxy silane marketed under the code Z6032 by Dow Corning Ltd.

The dried, cooled glass was mixed with a polyester resin polymer comprising 80% w/w A2622 and 20% w/w A2593 made by BP Chemicals Ltd., the weight of the resin mix was 180g giving a glass/resin ratio of 5.52 (84.6% glass). To this mix was added 4 mls of a 60% methyl ethyl ketone peroxide (MEKP) catalyst and 2 mls of 0.6% cobalt naphthenate promoter. The whole mix was poured and trowelled into a 7" × 7" × 5/8" mould of isilcone rubber on a sheet of polished glass.

Curing required 2 hours at room temperature after which the tile was removed from the mould and post cured at 105°C for 2 hrs. This tile had a high gloss randomly patterned surface showing predominantly the colour of the coarse particles and a background colour due to the smaller size fractions.

EXAMPLE 2.

The glass was crushed and ground as in Example 1 and formulated as follows:

| | | |
|---|---|---|
| Coarse | brown glass | 310 g. |
| | Green glass | 133 g |
| Medium | brown (3— 6 mesh) | 158 g |
| | green (6—12 mesh) | 79 g |
| | white (6—12 mesh) | 79 g |
| Fine | white (thro 85 mesh) | 234 g |

This mixture was pretreated with Dow Corning Ltd. silane Z6040.

The dried, cooled glass was mixed with an epoxy resin formulation (manufactured by Ciba-Geigy Ltd.) comprising 75 g GY250 resin, 43 g HY1341 GB hardener giving a glass/resin ratio of 8.3 (90.2% glass). Very thorough "trowelling" served to substantially remove all the air voids, and the tile had a very high gloss surface of considerable hardness when the mix was cast onto a glass supported 'Teflon' sheet.

EXAMPLE 3.

The glass was crushed and ground as before and formulated as follows:

| | |
|---|---|
| Coarse | 350 g white; |
| | 150 g brown; |
| Medium | 300 g green; and |
| Fine | 330 g white. |

The fine fraction, previously pretreated with Dow Corning Ltd. silane Z6040 was premixed with a resin mix supplied by British Industrial Plastics Ltd. and comprising 198 g of 'Beetle' (Registered Trade Mark) W2 urea-formaldehyde resin and 22 g of L5128 hardener. Pretreated coarse and medium fractions were then added and mixing completed.

The mix was trowelled into the mould on a waxed glass plate and allowed to cure out at room temperature. After 3—4 hrs. the tile was removed from the mould.

In this example, the tile as removed from the mould did not have an aesthetically pleasing surface and was diamond polished to remove a surface layer of resin and reveal the glass pattern beneath.

EXAMPLE 4.

Example 1 was repeated except that the formulation of glass and resin was changed slightly to provide a "sparkling" surface by the omission of the fine white glass dust.

The fine fraction was replaced by 12—60 mesh glass (1.40—0.250 mms) to give the following formulation:

| | | | |
|---|---|---|---|
| Coarse | 250 g | white; | |
| | 170 g | brown; | |
| Medium | 100 g | white | 3— 6 mesh; |
| | 100 g | brown | 3— 6 mesh; |
| | 120 g | white | 6—12 mesh; and |
| Fine | 30 g | white | 12—25 mesh; |
| | 30 g | white | 25—60 mesh. |

200 g polyester resin mix as in Example 1 giving a glass/resin ratio of 4.0 (80% glass).

This tile, as mentioned above, had a bright, sparkling highly reflective surface with pin points of reflection coming from the larger fine fraction.

Mixtures of these and other formulations can be cast into other than flat surface shapes in suitable moulds for producing, for example, bathroom and sanitary ware and fittings, kitchen furniture and working surfaces.

## EXAMPLE 5.

The glass was crushed and ground as previously described and formulated as follows:

| | | |
|---|---|---|
| Coarse | 99 g | green; |
| | 42 g | white; |
| Medium | 42 g | green; |
| | 42 g | white; |
| Fine | 93 g | |

and the resulting aggregate mixture was pretreated with Dow Corning Ltd. silane Z6032.

The dried, cooled glass was mixed with a polyester resin polymer comprising 80% w/w A 2622 and 20% w/w A 2593 made by BP Chemicals Ltd. The weight of resin mix was 65 g giving a glass/resin ratio of 4.89 (i.e. 83.0% glass).

To this mix was added 1.5 mls of 60% MEKP catalyst and 1.0 ml of cobalt 0.6% naphthenate promoter.

The mix was poured and trowelled into a 7" × 7" × 5/8" mould of silicone rubber on a sheet of wax polished glass. This quantity of mix left a space of 3/8 inch at the top of the mould and this was filled with a backing concrete mix comprising (in the order of mixing)

96 g water;
1.5 mls wetting agent;
100 g silica sand;
274 g Portland Cement, and
19 g Pilkingtons CemFIL (Registered Trade Mark) fibre.

The backing mix was poured and vibrated onto the uncured polyester/glass mix and 'trowelled' to provide a smooth flat surface.

The total curing time is determined by the concrete backing layer, and, in this example, the moulded mix was left to cure overnight in the mould, after which the complete tile was removed and cured for a further 24 hours in a water bath at 50°C.

The invention, therefore, includes an article when made in accordance with the foregoing description and including a backing layer. The backing layer may be selected for reinforcing purposes or it may be selected for economic reasons, namely, reducing the quantities and attendant costs of the resins, polymer, catalyst etc. The backing layer may, for example, be made from a compatible resin or polymer composition, or insulation material or concrete. The backing layer may, as desired, be reinforced using glass fibres, wire wool, metal turnings etc. In circumstances where it is required, for example, to decrease the thermal conductivity of an article, for example, a tile, the backing may include an insulating material. The insulating material may be in the form of a foam or the constituents of a foamable composition may be applied to the cured or uncured article (if tile) mix.

Tests carried out to ascertain the mechanical strength of the composites of glass and polyester resin according to the invention established that for a constant loading of glass (70%) in polyester (30%), both tensile stress and compressive stress exhibit a maximum in excess of those obtained for pure polyester resin when the grain size was in the range 44—85 mesh (0.355—0.180 mms.). Tests also indi-

cated that the pretreatment of the aggregate mixture of glass made a significant contribution to the increased tensile and compressive stresses.

Although specific reference has been made to the manufacture of tiles, pipes and sanitary ware, other articles may be moulded using the composition as described.

The use of glass aggregate for reinforcing or extending polymer resin produces a material which compares favourably with glass fibre reinforced plastics materials when subjected to compressive stress but unfavourably when subjected to tensile stress.

Glass aggregate particles and/or powders when compounded with resin possess a number of advantages, for example:

1. They give rise to composites as strong as the basic resin when due allowance is made of particle size, glass pretreatment to improve the resin of glass bond, and the relative ratios of glass/resin.
2. Working at glass to resin ratios in the range of 3.0 to 1.0 as against a glass fibre to resin ratio in the range of 0.3 to 1.0 a considerable saving in resin for a given application is achieved.
3. Use of the large glass aggregate fraction acts as a good exotherm adsorber which allows thick sections to be case in a suitable mould rapidly and accurately without fear of exothermic cracking.
4. Where the modest strengths of these composites are adequate, casting techniques are much less time consuming than the laborious laying up techniques of glass fibre laminating.
5. Penetration of the composite by corrosive and other liquids is less likely with particles than with fibres which propagate the ingress of moisture by so-called "wicking" along their length which eventually gives rise to delamination. When compared with fibres, particles are of short path length and are each surrounded or encapsulated by a resin surface.

Pigments and fillers may be added to or milled onto glass powder to produce castings of uniform colour.

As mentioned previously, the glass aggregate is first pretreated with a silane surface treating agent to increase the resin to glass bonding and thereby enhance mechanical strength. Alternatively a chromium/acrylic complex may be employed as the pretreating agent.

Mixing of the casting mixture is carried out in a conventional laboratory or kitchen-type mixer depending on the mix viscosity and batch size and the catalyst and the promoter are added into the mix immediately prior to casting.

The glass aggregate may of itself be coloured but, where the glass is clear and colouring is required, application of a colourant is preferably carried out after pretreatment with the coupling agent.

Suitable pigments which can be used include Monastral (Registered Trade Mark) Fast Blue, Monolite (Registered Trade Mark) Red (I.C.I.); Cibanone (Registered Trade Mark) Mellow G.C.M.D., Chlorazol Fast Yellow B.S. (Ciba-Geigy) and Ferric Oxide and slate dust.

## EXAMPLE 6.

Pretreatment of the aggregate for all aspects of the invention may be carried out by the following method:

The glass is weighed into a mixing vessel as for the aqueous treatment method previously described. 100 gms of glass of assorted sizes is tumbled with 5 gms of Z 6032 (a silane composition manufactured by Dow Company) 40% solids in methanol, for 15 to 30 minutes. The glass is then dried at a temperature not exceeding 105°C for 15 to 20 minutes. This glass is then ready for compounding with resins prior to casting or forming.

Alternatively, where colourant is to be added to the glass, 1000 gms of pretreated, dried and cooled glass can be mixed with not more than 10 gms of epoxy resin mix (e.g. Araldite (Registered Trade Mark) MY 753/HY956) or a polyester resin (e.g. BP A2622 or A2593) or any suitable low viscosity room temperature or oven-cured resin system and a colouring pigment added to give a desired depth of colour. The surface coated, coloured glass may then be finally cured in an oven.

WHAT WE CLAIM IS:—

1. A method of preparing an article from a composition comprising:

(a) formulating a mixture of coarse, medium and fine aggregates (as herein defined);
(b) pretreating the mixture (a) with a coupling agent;
(c) mixing the pretreated mixture (of (b)) with a curable resin and a curing catalyst for curing the curable resin, and
(d) forming the resulting mixture (of (c)) into an article and curing or allowing the same to cure.

2. A method according to claim 1 including adding to mixture (a) a further mixture comprising additional fine aggregate (as hereindefined) which is pretreated with a coupling agent, polymer, polymerisation and/or colouring agent, and a curing catalyst.

3. A method according to claim 1 wherein the mixture (a) comprises 44.3 wt %, 26.5 wt % and 29.2 wt % of coarse, medium and fine aggregate respectively.

4. A method according to claim 1, 2 or 3 wherein the coupling agent is a silane composition.

5. A method according to claim 4 wherein the silane composition is an aqueous solution of trimethoxy silane having a pH within the range 4—6.

6. A method according to claim 5 including an additional step (b1) wherein the silane treated mixture of step (b) is dried by heating and cooled or allowed to cool prior to carrying out step (c).

7. A method of making an article according to any preceding claim wherein step (d) is effected on a backing layer made from a compatible resin or polymer composition, or insulation material or concrete.

8. A method according to claim 7 wherein the backing layer is reinforced.

9. A method of making an article in accordance with any one of Examples 1 to 6.

10. An article when made in accordance with any one of claims 1 to 9.

11. An article substantially as hereinbefore described and with reference to any one of Examples 1 to 6.

WITHERS & ROGERS,
Chartered Patent Agents,
4, Dyer's Buildings,
Holborn, London, EC1N 2JT.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.